Contribution from the Department of Chemistry,
The University of Akron, Akron, Ohio 44325

Effects of Substituents on the Spectroscopic Properties of Tetradentate Ligand–Oxovanadium(IV) Complexes

H. A. KUSKA* and PANG-HSIONG YANG

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Oxovanadium(IV) chelates of the tetradentate Schiff base ligands *N,N'*-bis(2-hydroxybenzophene)ethylenediamine, *N,N'*-bis(5-methyl-2-hydroxybenzophene)ethylenediamine, *N,N'*-bis(4-methyl-5-chloro-2-hydroxybenzophene)ethylenediamine, and *N,N'*-bis(5-chloro-2-hydroxybenzophene)ethylenediamine have been prepared. Electron-withdrawing groups reduce the V═O infrared stretching frequency and increase the electron spin resonance hyperfine splitting value. Linear correlations of both parameters with the Hammett σ factors for the substituents were found. Extended Hückel molecular orbital calculations were able to simulate both effects. The experimental optical transition energies were relatively independent of substituent.

Introduction

As reviewed elsewhere[1,2] there have been a considerable number of spectroscopic studies on oxovanadium(IV) complexes. The initial expectations were optimistic. Since the vanadium valence-shell electronic configuration is d^1 and since the crystal field is dominated by the strong V═O interaction, a consistent easily interpretable set of experimental data was expected. In general, this optimism has not been substantiated. One possible reason for the lack of self-consistency in previous sets of spectroscopic data is that the three-dimensional local geometry around the vanadium may have changed from complex to complex (possibly by the vanadium moving out of the equatorial ligand plane). In order to remove this ambiguity we have prepared and characterized a series of substituted tetradentate ligand complexes, VO(R_1–R_2–hbp)$_2$en. A structural representation of the complexes studied and their abbreviations are given in Figure 1. Since the utilization of variable substituents is only on the phenyl groups, any difference in spectroscopic properties should be due to the substituent effect only and not to a difference in the local symmetry around the vanadium atom.

Experimental Section

Materials. 5-Chloro-2-hydroxybenzophenone, 5-chloro-2-hydroxy-4-methylbenzophenone, *o*-hydroxybenzophenone, and 2-hydroxy-5-methylbenzophenone were obtained from the Aldrich Chemical Co., ethylenediamine was obtained from Matheson Coleman and Bell Co., and oxovanadium(IV) sulfate was obtained from Ventron Co.

Preparations. Ligands. To a hot methanol solution of 0.02 mol of the substituted benzophenone, 0.011 mol of the appropriate diamine was added. After stirring, heating, and refluxing of the resulting mixture, a yellow crystal was obtained.

Vanadyl(IV) Complexes. To a methanol–acetone–2,2-dimethoxypropane solution of 0.005 mol of the correspondent ligand, 0.005 mol of oxovanadium(IV) sulfate was added. The mixture was heated on a hot plate. The resulting precipitate was collected by filtration, washed with methanol, and dried in vacuo. The analytical data, melting points, and colors are given in Table I.

Measurements. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Infrared spectra of the complexes were recorded as chloroform solutions in KBr cells and as mineral oil mulls between AgCl plates on Perkin-Elmer 521 and/or 337 infrared grating spectrophotometers. The chloroform was purified by passing it through an activated alumina column to remove the ethanol.

The ESR spectra of the complexes in the solvents were carried out on a Strand-Magnion, Varian hybrid spectrometer. The solution spectra were run in the ethanol-free chloroform. The anisotropic data were obtained in cellulose nitrate.

Digital electronic absorption spectra were obtained from a Cary 17 spectrophotometer and resolved into Gaussian components by the use of the Fortran program BIGAUSS written by R. G. Cavell.[3]

Theoretical Calculations. The extended Hückel method was used, as described previously.[4] The actual *x, y, z* coordinates, as determined in an x-ray study[5] for [bis(acetylacetone) ethylenediimine]oxovanadium(IV), VO(acen), were used. In any extended Hückel molecular orbital calculation that involves C–CH_3 groups one has the problem of how to allow for rotation around the C–C single bonds. The use of static *x, y, z* positions for the hydrogens may result in molecular orbitals which are unduly influenced by conjugation with the hydrogen atomic orbitals. This is due to the use of the overlap integral in the off-diagonal matrix element approximation. To minimize this effect C^{3-} groups were used in place of the four CH_3 groups. The orbital exponents used for the C^{3-} group are 2.30 (2s) and 2.00 (2p). These larger than normal values were chosen to decrease the overlap integrals between the C^{3-} groups and the rest of the molecule. The calculation procedure consisted of varying the C^{3-} H_{ii} values and keeping the H_{ii} values for the other atoms constant. The purpose of this approach is to examine the effects on the molecular properties of the pseudogroup, C^{3-}, with different electronegativities (H_{ii} values).

Results

Infrared Studies. The V═O stretching frequencies of the oxovanadium(IV) complexes in mineral oil mull and in chloroform are given in Table II. The stretching frequencies fall into two regions, ~880 and ~980 cm^{-1}. Previously, the low V═O stretching frequency region from around 850 to 900 cm^{-1} has been considered to be an indication of oxygen bridging, V–O–V, polymeric chain formation.[6,8,18] However, a recent x-ray study by Pasquali et al.[19] demonstrates that other solid-state effects can cause this shift.

The mull IR data show that the V═O stretching frequencies of VO(5-Cl-hbp)$_2$en and VO(4-CH_3-5-Cl-hbp)$_2$en appear at 881 and 879 cm^{-1}, respectively. The most obvious difference between the "normal" and the low-frequency complexes is the presence of the electron-withdrawing Cl groups in the ligands of the latter complexes. Similar oxygen low V═O stretching frequencies have been found in the vanadyl(IV) complexes of salicylidenimine,[7,19] monothio-β-diketone,[8] and dithiophosphinic acids[9] with electron-withdrawing substituents, while it does not occur in those with electron-donating groups.[7,9,10,19]

The substituent groups on the phenolic phenyl rings may affect both the phenolic oxygen and the imine nitrogen electron densities. Due to the longer distance the substituent effect is expected to be smaller on the imine nitrogens than on the phenolic oxygens. As can be seen in Figure 2, the question of what relative weights to give the oxygen and nitrogen substituent effects turns out to be academic as both the complete neglect of the nitrogen term and the equal weight approximation give equally valid correlations.

The V═O stretching frequencies increased with an increase of the Hammett σ factors (electron-withdrawing ability) of the substituent groups. This is consistent with the calculated dependence of the vanadium–oxygen overlap population on the electronegativity of the substituents (Table III). From an examination of the overlap populations of the individual V–O bonds, it appears that the increase is due mainly to an increase in the V–O π-bond populations. Surprisingly, the dependence observed for substituted vanadyl acetylacetonates[11]

Table I. Physical Characterization Data

Complex	% C		% H		% N		Mp,[a] °C	Color
	Calcd	Found	Calcd	Found	Calcd	Found		
$VO(hbp)_2en$	69.28	69.09	4.57	4.61	5.65	5.65	>300	Green
$VO(5\text{-}CH_3\text{-}hbp)_2en$	70.17	69.98	5.10	5.06	5.46	5.30	>300	Green
$VO(5\text{-}Cl\text{-}hbp)_2en$	60.67	60.50	3.64	3.79	5.05	5.05	>300	Gold
$VO(4\text{-}CH_3\text{-}5\text{-}Cl\text{-}hbp)_2en$	61.87	61.99	4.15	4.25	4.81	4.73	294-297	Gold

[a] Uncorrected.

Table II. The V=O Stretching Frequencies of the Complexes[a]

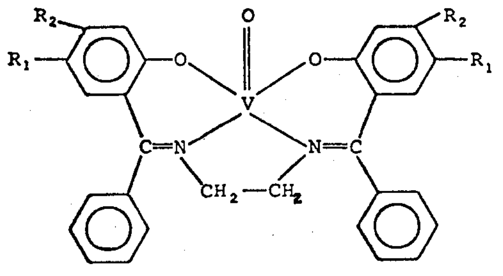
Complex	Mineral oil mull	$CHCl_3$
$VO(5\text{-}Cl\text{-}hbp)_2en$	881	983
$VO(4\text{-}CH_3\text{-}5\text{-}Cl\text{-}hbp)_2en$	879	981
$VO(hbp)_2en$	980	980
$VO(5\text{-}CH_3\text{-}hbp)_2en$	980	978

[a] Units are cm^{-1}; standard deviation ±1 cm^{-1}.

Table III. Theoretical V=O Bond Order Dependence on Substituent Electronegativity

% increase in H_{ii} values[a]	% increase in total V=O bond order	% increase in σ V=O bond order	% increase in π V=O bond order
2.9	0.24	0.10	0.36
6.6	0.46	0.13	0.72
13.1	0.67	0.16	1.09
31.7	1.20	0.38	1.86
72.8	1.43	0.51	2.17

[a] The greater the increase the more electronegative the substituent (C^{3-} group).



R1	R2	Compound
H	H	$VO(hbp)_2en$
Cl	H	$VO(5\text{-}Cl\text{-}hbp)_2en$
Cl	CH_3	$VO(4\text{-}CH_3\text{-}5\text{-}Cl\text{-}hbp)_2en$
CH_3	H	$VO(5\text{-}CH_3\text{-}hbp)_2en$

Figure 1. Structural representation of the substituted *N,N′*-bis(2-hydroxybenzophene)ethylenediaminooxovanadium(IV).

is the opposite of the dependence observed in this series of complexes.

Electron Spin Resonance. The isotropic ESR parameters for the vanadyl(IV) complexes are given in Table IV. Also given are the covalency parameters calculated from eq 1 with

$$N_{xy}^2 = \frac{|A|}{PK} + \frac{g - 2.0023}{K} \qquad (1)$$

$K = 0.759$ and $P = 0.01195$.

N_{xy}^2 is the coefficient of the d_{xy} atomic orbital in the in-plane π molecular orbital which contains the unpaired electron. K is the Fermi contact term and P is the dipole term.[12]

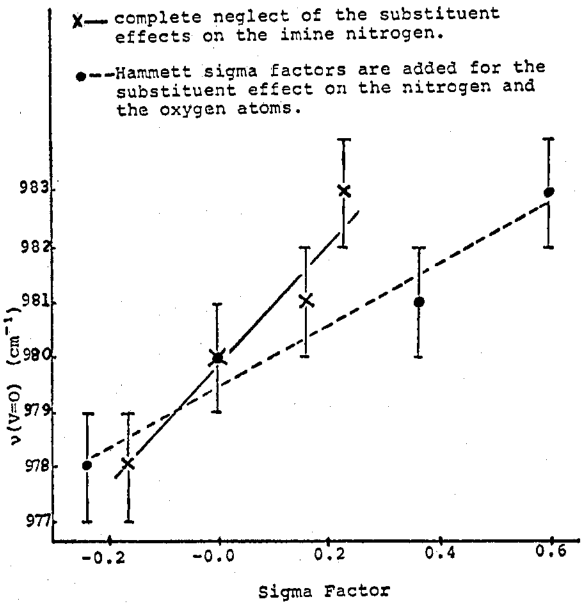


Figure 2. V=O stretching frequency vs. the Hammett σ factor for substituted $VO(R_1\text{–}R_2\text{–}hbp)_2en$ complexes.

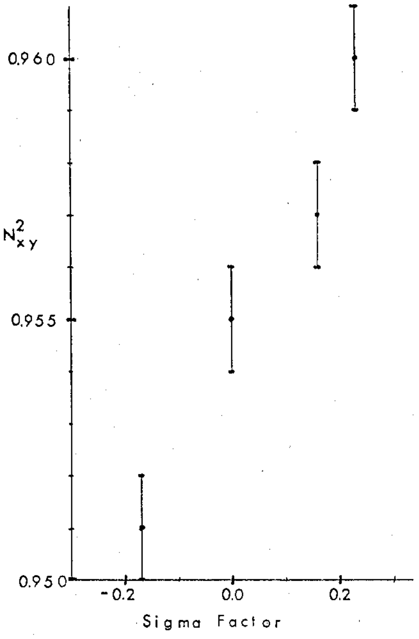


Figure 3. ESR-determined N_{xy}^2 molecular orbital coefficient vs. the Hammett σ factor for substituted $VO(R_1\text{–}R_2\text{–}hbp)_2en$ complexes.

A plot of the N_{xy}^2 values vs. the σ factors is given in Figure 3. The σ factors used here are the effects on the phenolic oxygen only since Figure 2 shows that they have the same trend when the effects on the imine nitrogen are also considered. A linear correlation exists between the N_{xy}^2 values and the σ factors. A more electron-withdrawing substituent gives a larger atomic orbital coefficient. This dependence is in the

Table IV. Isotropic ESR Parameters and Calculated Parameters

Compd	g	$10^{-4}A$, cm^{-1}	N_{xy}^2 [c]	Vanadium charge[d]
VO(5-Cl-hbp)$_2$en[b]	1.975 ± 0.001[a]	90.3 ± 0.1	0.960 ± 0.001	1.607
VO(4-CH$_3$-5-Cl-hbp)$_2$en[b]	1.975 ± 0.001	90.1 ± 0.2	0.957 ± 0.001	1.595
VO(hbp)$_2$en[b]	1.975 ± 0.001	89.9 ± 0.1	0.955 ± 0.001	1.583
VO(5-CH$_3$-hbp)$_2$en[b]	1.975 ± 0.001	89.5 ± 0.1	0.951 ± 0.001	1.558

[a] Standard deviation. [b] In chloroform. [c] Calculated from eq 1. [d] Calculated from eq 3.

Table V. Anisotropic ESR Parameters

Compd	$g_\parallel$	$g_\perp$	$A_\parallel$[d]	$A_\perp$[d]	Ref
VOF$_5^{3-}$	1.937	1.977	178.5	64.5	*a*
VO(acac)	1.943	1.979	170.5	61.5	*b*
VO(acac)en	1.954	1.984	166	57.4	*b*
VO present series	1.956	1.982	157.5	54	*c*
VO(por)	1.961	1.988	159.1	55.8	*b*
VO(CN)$_5^{3-}$	1.9711	1.984	137	47.2	*b*

[a] P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 49, 3912 (1968). [b] See Table V of ref 12. [c] This work. [d] Units of 10^4 cm^{-1}.

same direction as that observed for the substituted acetylacetonates[13] but the dependence is an order of magnitude larger for the acetylacetonates. It appears that the assumption of a constant in-plane π covalency for the present series would be an appropriate first-order approximation when attempting to determine the effects of the substituents on the overall electron density on the vanadium.

In the above application of eq 1 it was assumed that the changes in the ESR A values were due only to changes in the covalency N_{xy}^2 and not to changes in P and/or K. For a closely related series such as this one, the constant Fermi contact term, K, approximation is probably valid. However, since the dipole term P is a function of the total vanadium charge, it is possible that it would be a better approximation to consider N_{xy}^2 constant and to relate the charge on the vanadium to the isotropic ESR A value. The relation of P to the charge is[14]

$$P = 8.57 \times 10^{-3} + 2.1385 \times 10^{-3} \times \text{charge} \qquad (2)$$

Combining eq 1 and 2 yields

$$\text{charge} = |A|/(2.1385 \times 10^{-3}(KN_{xy}^2 - g + 2.0023)) - 4.007 \qquad (3)$$

The calculated charges are given in Table IV. The maximum change in the vanadium charge is 0.049 of an electron.

The anisotropic ESR data were obtained from random orientation spectra. This involved fitting the experimental spectrum to a computer-generated one. Especially in the $A_\perp$, $g_\perp$ region, it is difficult to distinguish between fits when $A_\perp$ is varied by less than ±1 G. Since the substituent effect is less than this uncertainty, only one set of values is given for the series, Table V. As can be seen from the anisotropic data listed for other representative vanadyl complexes (also see Table V in ref 12), the present compounds appear to be somewhat similar in bonding properties to the porphyrin type complexes. The lack of any detectable splitting of the $A_\perp$ and/or $g_\perp$ terms is surprising since, as discussed in the following section, the $xy \rightarrow xz, yz$ transitions appear to be split by about 0.2 μm^{-1}.

Optical Studies. The Gaussian analysis of the visible portion (1.0–2.5 μm^{-1}) of the optical absorption spectrum in chloroform yields four peaks at 1.28–1.31, 1.52–1.54, 1.72–1.73, and ~2.1 μm^{-1}. A typical Gaussian analysis of the optical spectrum in the visible portion is given in Figure 4. The absorption maxima and the oscillator strengths are given in Table VI. Because of an intense charge-transfer band, the energy of the 2.1-μm^{-1} band was only able to be quantitatively determined for one of the complexes.

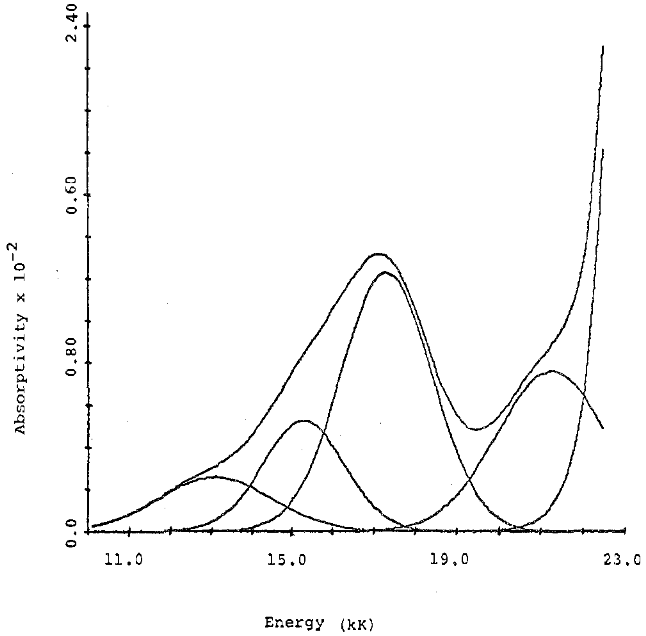


Figure 4. Gaussian analysis of VO(hbp)$_2$en in the chloroform optical spectrum.

Table VI. Optical Spectra of VO(R$_1$-R$_2$-hbp)$_2$en in Chloroform[a]

	VO(5-Cl-hbp)$_2$en		
12.8 ± 0.1[c]	15.3 ± 0.1	17.2 ± 0.1	
(3.2 ± 0.1)[d]	(5.6 ± 1.7)	((1.3 ± 0.2) × 10)	*b*
	VO(4-CH$_3$-5-Cl-hbp)$_2$en		
12.8 ± 0.1	15.4 ± 0.1	17.3 ± 0.1	
(3.3 ± 0.2)	(8.5 ± 0.5	((1.3 ± 0.1) ×10)	*b*
	VO(hbp)$_2$en		
13.0 ± 0.1	15.2 ± 0.1	17.3 ± 0.1	21.3 ± 0.1
(3.7 ± 0.3)	(5.3 ± 0.4)	((1.6 ± 0.1) × 10)	(3.3 ± 0.9)
	VO(5-CH$_3$-hbp)$_2$en		
13.1 ± 0.1	15.2 ± 0.1	17.2 ± 0.1	
(3.5 ± 0.3)	(6.0 ± 0.5)	((1.5 ± 0.1) × 10)	*b*

[a] Units are cm^{-1} × 10^3. [b] Peak present but position could not be quantitatively determined. [c] Standard deviation. [d] Oscillator strength ×10^4.

Table VII. Calculated Charges on Vanadium and Five-Coordinated Ligand Atoms for VO(C^{3-}-pdo)$_2$en

% increase in H_{ii} values[a]	Q(V)	Q(=O)[b]	Q(–O)[c]	Q(N)
0.0	1.7442	−0.5586	−0.7691	−0.7599
2.9	1.8806	−0.5566	−0.7780	−0.7593
6.6	1.9342	−0.5541	−0.7831	−0.7588
13.1	1.9700	−0.5509	−0.7879	−0.7586
31.7	2.0049	−0.5456	−0.7991	−0.7622
72.8	1.9997	−0.5464	−0.8327	−0.7888

[a] The greater the increase the more electronegative the substituent (C^{3-} group). [b] Vanadyl oxygen. [c] Ligand oxygen.

The present compounds are similar to the substituted bissalicylaldehyde 1,2-diamine complexes studied by Pasini and Gullotti[15] and by Farmer and Urbach.[16] Both of these

Table VIII. Calculated Dependence of the Optical Transitions on the Position of the Vanadium Relative to the Equatorial Plane

Dist to eq plane, Å	E(I)[a]	N_{xz}[b]	$N_{x^2-y^2}$	N_{yz}	E(II)	N_{xz}	$N_{x^2-y^2}$	N_{yz}	E(III)	N_{xz}	$N_{x^2-y^2}$	N_{yz}
0.39	6.17	0.07	−0.03	0.82	7.21	0.82	−0.03	−0.14	17.7	0.17	0.46	0.09
0.59[c]	7.89	0.14	−0.02	−0.83	8.68	−0.83	0.06	−0.10	15.2	0.14	0.68	0.01
0.79	8.78	−0.39	0.22	0.73	9.51	−0.75	0.09	−0.41	11.9	0.22	0.73	−0.17
0.99	9.99	0.36	0.40	−0.64	9.42	−0.76	−0.01	−0.41	7.47	0.24	−0.69	−0.37

[a] E(I), E(II), and E(III) are the energies of the first three predicted optical transitions; units are $\mathrm{cm}^{-1} \times 10^3$. [b] N_{xz}, $N_{x^2-y^2}$, and N_{yz} are the values of the indicated vanadium atomic orbital coefficients in the molecular orbital which receives the electron in the optical transition. [c] Experimental value for VO(acac)en.

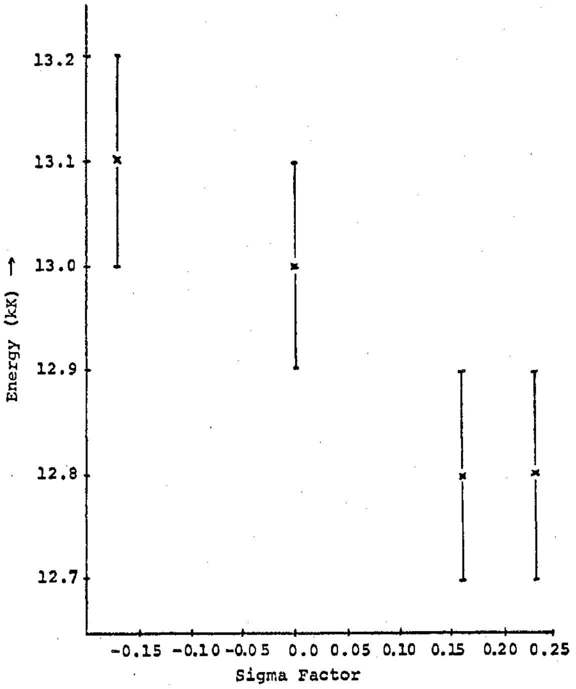


Figure 5. The 1.28–1.31-$\mu\mathrm{m}^{-1}$ absorption band vs. the Hammett σ factor for substituted VO(R_1–R_2-hbp)$_2$en complexes. ($1\ \mu\mathrm{m}^{-1} = 10$ kK.)

studies confirm the presence of a transition at about 2.1 $\mu\mathrm{m}^{-1}$ which is thought to be the $xy \rightarrow z^2$ transition. The two studies do not agree, however, on the presence of three additional visible bands. In general Pasini and Gullotti found three additional bands while Farmer and Urbach reported only two.

The effects of the substituents on the energies of the transitions are of the same magnitudes as the experimental precisions for the 1.5- and 1.7-$\mu\mathrm{m}^{-1}$ bands. For the 1.3-$\mu\mathrm{m}^{-1}$ band a small real dependence appears to exist; see Figure 5. Electron-donating groups increase the energy of this transition. At first we were tempted to assign this band as the $xy \rightarrow x^2 - y^2$ with the assumption that an electron-donating group (negative σ factor) would increase the electron density on the nitrogen and oxygen equatorial ligand atoms. However, the other experimental and extended Hückel calculated data are inconsistent with this assumption.

The most consistent assignment for the bands is to assign the 1.3- and 1.5-$\mu\mathrm{m}^{-1}$ bands as the split $xy \rightarrow xz, yz$ transitions and the 1.7-$\mu\mathrm{m}^{-1}$ band as the $xy \rightarrow x^2 - y^2$ transition. If this assignment is correct, one must accept an unusually large splitting of the xz, yz levels. However, this feature is consistent with a distortion which moves the geometry toward a trigonal-bipyramidal configuration.[19] Two recent extended Hückel calculations on C_{2v} distorted square-pyramidal geometry vanadyl complexes[4,17] did result in a xz, yz splitting of about 0.2 $\mu\mathrm{m}^{-1}$, and both calculations placed the xz, yz levels below the $x^2 - y^2$. In one of the above calculations the ordering was supported by intensity calculations (the $xy \rightarrow x^2 - y^2$ transition was calculated to be more intense than the $xy \rightarrow xz$ or yz).[4]

Theoretical Studies. As can be seen from Table VII, the predicted effect of an electron-donating group is to decrease the nitrogen and oxygen equatorial ligand electron densities. In order to understand what causes this unexpected behavior the characteristics of the individual σ and π bonds were examined. The electron densities in the vanadium–ligand σ and out-of-plane π bonds increase with increasing electronegativities of the C^{3-} groups, while the electron densities in the vanadium–ligand in-plane π bonds remain relatively constant.

As discussed in the Optical Studies section, there appears to be an unusually large energy splitting of the normally degenerate xz and yz molecular orbitals. To test whether this splitting could be due to the vanadium being out of the equatorial plane, the extended Hückel molecular orbital calculations were repeated with distortions of this type; see Table VIII. Rather than resulting in a simple moving of the $x^2 - y^2$ and/or the xz and yz levels, the displacement resulted in a significant amount of mixing of the three vanadium atomic orbitals in the molecular orbitals. The major energy effect is an eventual crossing of the original $xy \rightarrow xz, yz$ bands and the $xy \rightarrow x^2 - y^2$ band.

As discussed in a recent paper,[14] we have developed a computer program which utilizes the anisotropic electron spin resonance data to determine the approximate ranges of the optical transition energies which are consistent with the ESR data. For the present compounds, this procedure predicts a range of 6000–9000 cm^{-1} for the $xy \rightarrow xz, yz$ transitions and a range of 16 500–26 500 cm^{-1} for the $xy \rightarrow x^2 - y^2$ transition. As also discussed in the original paper, one would expect that the relative predicted magnitudes are significant ($E_{xy \rightarrow x^2-y^2} > E_{xy \rightarrow xz,yz}$).

Registry No. VO(hbp)$_2$en, 62906-11-0; VO(5-CH_3-hbp)$_2$en, 62906-10-9; VO(5-Cl-hbp)$_2$en, 62906-09-6; VO(4-CH_3-5-Cl-hbp)$_2$en, 62906-08-5.

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